CENTRAL RESEARCH LABORATORY

THE BORDEN CHEMICAL COMPANY

A Division of The Borden Company

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Study Leading to the Development of
HIGH TEMPERATURE RESISTANT ADHESIVES
QUARTERLY PROGRESS REPORT NO. 2
1 October 1961 - 31 December 1961
CONTRACT NO. DA-36-034-ORD-3501-RD

For: Picatinny Arsenal, Dover, New Jersey

By: Central Research Laboratory
The Borden Chemical Company
Philadelphia 24, Pa.

STUDY LEADING TO THE DEVELOPMENT OF

HIGH TEMPERATURE

RESISTANT ADHESIVES

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Central Research Laboratory
The Borden Chemical Company
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PICATINNY ARSENAL
Dover, New Jersey

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FOREWORD

This report covers the work under Contract No. DA-36-034-ORD-3501-RD titled "High Temperature Resistant Adhesives", from October 1, 1961 to December 31, 1961. The personnel on this project are Dr. K. C. Tsou, and Mr. H. E. Hoyt, assisted by Mr. N. Zucker and Mr. C. Guinosso. Project Officer has been Mr. M. Bodnar of Picatinny Arsenal. Physical testing has been performed by the Physical Testing group under the supervision of Dr. G. Kitazawa.

Approved by: Dr. B. D. Halpern
Research Director
The Borden Chemical Company

SUMMARY

The preparation of brominated polyxylenol was repeated by the use of N-bromosuccinimide and the resultant polymer was converted to the phthalimide derivative with the aid of dimethylformamide as solvent. The distribution of bromine and nitrogen in these polymer samples has now been determined.

A scale-up procedure for 2-methyl-6-allyl-4-bromophenol has been developed to permit subsequent polymerization and copolymerization with 2,6-dimethyl-4-bromophenol.

Homopolymerization and copolymerization conditions have been investigated and copolymers of 2-methyl-6-allyl-4-bromophenol and 2,6-dimethyl-4-bromophenol have been prepared in good yield. The 50:50 copolymer was chosen for further study in Phase II of the adhesive test.

Polymerization of 2-methyl-4-bromophenol does give a polymeric material in low yield. Various possible structures are discussed.

In order to further investigate the possibility of a polyether strand type polymer based on o-cresol novolac, an unambiguous intermediate, 4,4'-dibromo-2,2'-dimethyl-6,6'-bismethylenephenol was prepared successfully. Preliminary polymerization attempts, however, were not successful and a dimer was isolated. The structure of this dimer has been assigned.

Testing procedure has now been standardized to include a laminated glass cloth to insure constant thickness in glue lines. Conditions for solvent coating have been investigated and long-time air-drying gave the best result. Using this method, the polyxylenol gives an average of 3150 psi for five samples at room temperature. After heating at 500° F. for 30 minutes and test at the same temperature, the strength drops to 129 psi. The evaluation of the copolymer 50:50, however, gives only 1100 psi at room temperature, but drops only to 265 psi, at 500° F. for 30'.

CONCLUSIONS

At 500° F. the copolymer (50:50) of 2,6-dimethyl-4-bromophenol and 2-methyl-6-allyl-4-bromophenol retains a greater percentage of its room temperature shear strength when compared to polyxylenol. It is likely that the unsaturation in the allyl group result in some cross-linking and therefore this approach offers encouragement for higher strength at test temperature.

The molecular weight of the copolymer should be improved to give higher initial strength and at the higher testing temperature. Synthesis and modification work should be continued in this series. Emphasis should be placed on the epoxidation of the allyl-containing copolymer.

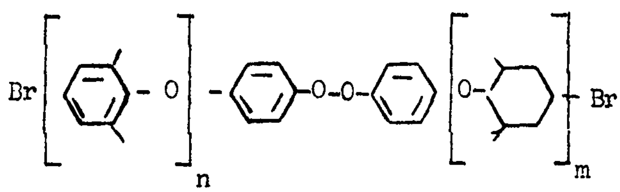
The amine-cured bromo-substituted polyxylenols are too brittle to be of any further interest to the adhesive program. This phase of chemical modification is therefore to be temporarily discontinued.

DISCUSSION

I. CHEMICAL MODIFICATION OF POLYXYLENOLS

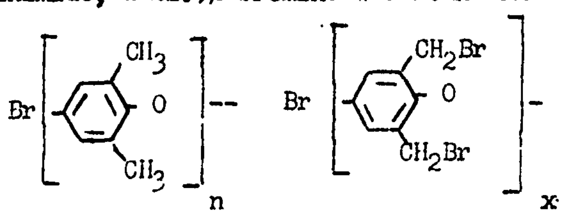
A. Brominated Polyxylenol:

In the previous reports, it was mentioned that the poly2,6-dimethyl-1,4-phenylene oxide can be brominated with N-bromosuccinimide. Based on the bromine analysis now obtained and a better understanding of the termination step of the polymerization of such polymers, it is appropriate to re-examine this intermediate. A typical polyxylenol or poly-(2,6-dimethyl)-1,4-phenylene oxide was used which was found to have 3.5% bromine. For chain termination we now favor the mechanism of coupling of two long chain radicals



(see Discussion and Mech. in Section 7)

Using this concept the molecular weight can be calculated by 2×80 M.W. $= 0.035$ to be 4580, or a D.P. = 37. When this material was brominated with N-bromosuccinimide, a 21.9% bromine was found in the final product.

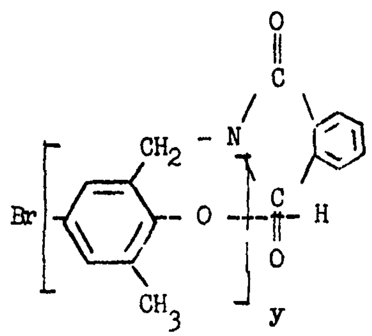


Using the equation $$\text{Fraction Br} = \frac{2 \times 80 + 80X}{2 \times 80 + 120\ (37) + 79X} = 0.219$$

where X = no. of methyl group substituted, one can calculate $X = 1.35$ or $13.5/2 \times 37 = 18.2\%$ of available methyl groups were now substituted.

B. Replacement of the Bromine by the Phthalimide Group:

In previous reports, difficulties in forming the phthalimido group were mentioned. It has now been found possible to carry out this step in a more polar solvent such as dimethyl formamide and a material containing 2.27% N and 12.99% bromine was obtained by analysis. If one uses the N value, then one may calculate the number of bromine on the side chain replaced by the phthalimido group to be 10-11, based on the following equation:



$$\text{Fraction N} = \frac{14\,y}{23(120 + (14-y)\ (208) + 160 + y(265)} = 0.0227$$

where y = number of phthalimido group. However, based on the bromine data, y is calculated to be 6. Therefore one may tentatively conclude that under the present conditions, about 44-76% of the bromine on the side chain are replaced by the phthalimido group. (If the termination step were not bi-radical coupling and there is only one Br atom per chain, then the bromine - N analysis would give closer agreement. However, we are not able to justify molecular weight determinations if this is done.)

C. Further Reactions of the Modified Materials:

The reaction of the brominated xylenol with ammonia was expected to yield cross-linked material. An infusible product (700° F.) was obtained which was, however, too brittle to be of any interest in our program.

The partial hydrolysis of phthalimido group by alkali was attempted and only cross-linked material was obtained. The reaction of hydrazine with the phthalimido group to introduce amino group was not attempted as we are still hopeful of carrying the reaction to a more complete stage.

2. PREPARATION OF 2-METHYL-4-BROMO-6-ALLYL PHENOL

The procedure for carrying out the Claisen rearrangement of 2-methyl-4-bromophenyl allyl ether to the phenol was reported in the first Quarterly Progress Report (page 12). However, the scale-up of the procedure to larger batch was not reproducible and numerable difficulties were encountered, especially in the control of the exotherm that accompanies the rearrangement. This was finally made possible by the simultaneous addition of such low boiling inert solvent as hexane. The details are to be found in the experimental part.

3. POLYMERIZATION OF 2-METHYL-4-BROMO-6-ALLYL PHENOL

2-Methyl-4-bromo-6-allyl phenol was polymerized under various conditions, and the results are summarized in Table Ia and Ib in the experimental section. Purity of the starting material is essential here as a small amount of either 2-methyl-4-bromo-phenyl allyl ether or other side reaction products lower the molecular weight and the yield appreciably because of the competitive allyl group in the radical propagation process.

It is necessary to initiate the reaction below 10° C. (higher temperature lowers the yield and m.w. of the product), and use high speed agitation to insure good dispersion of the benzene and caustic solution. The infrared spectra of the polymer ("MAP" polymer) shows distinct allyl band (Figure 1).

The aging properties of the allyl polymer were checked by comparing the molding temperature initially and after standing at room temperature for 71 days. The results (see Experimental section) indicate, contrary to results of others, that the cross-linking of allyl group does not take place at room temperature in the samples we tested.

4. COPOLYMERIZATION OF 2-METHYL-4-BROMO-6- ALLYL PHENOL AND 2,6-DIMETHYL-4-BROMO-PHENOL

The preparation of the copolymer follows essentially the same procedure as that used in the preparation of the homopolymer. The different copolymer ratios are determined only by the ratio of the corresponding phenol used and subsequently by the intensity of the allyl band in the infrared spectra (see Fig. 1). High yields and low recoveries of material in the benzene-methanol filtrate assured substantially complete conversion of the phenols to polymer. Tentative structure proof of the copolymer has been made by its infrared spectra but unequivocal proof is still needed to rule out homopolymer formation.

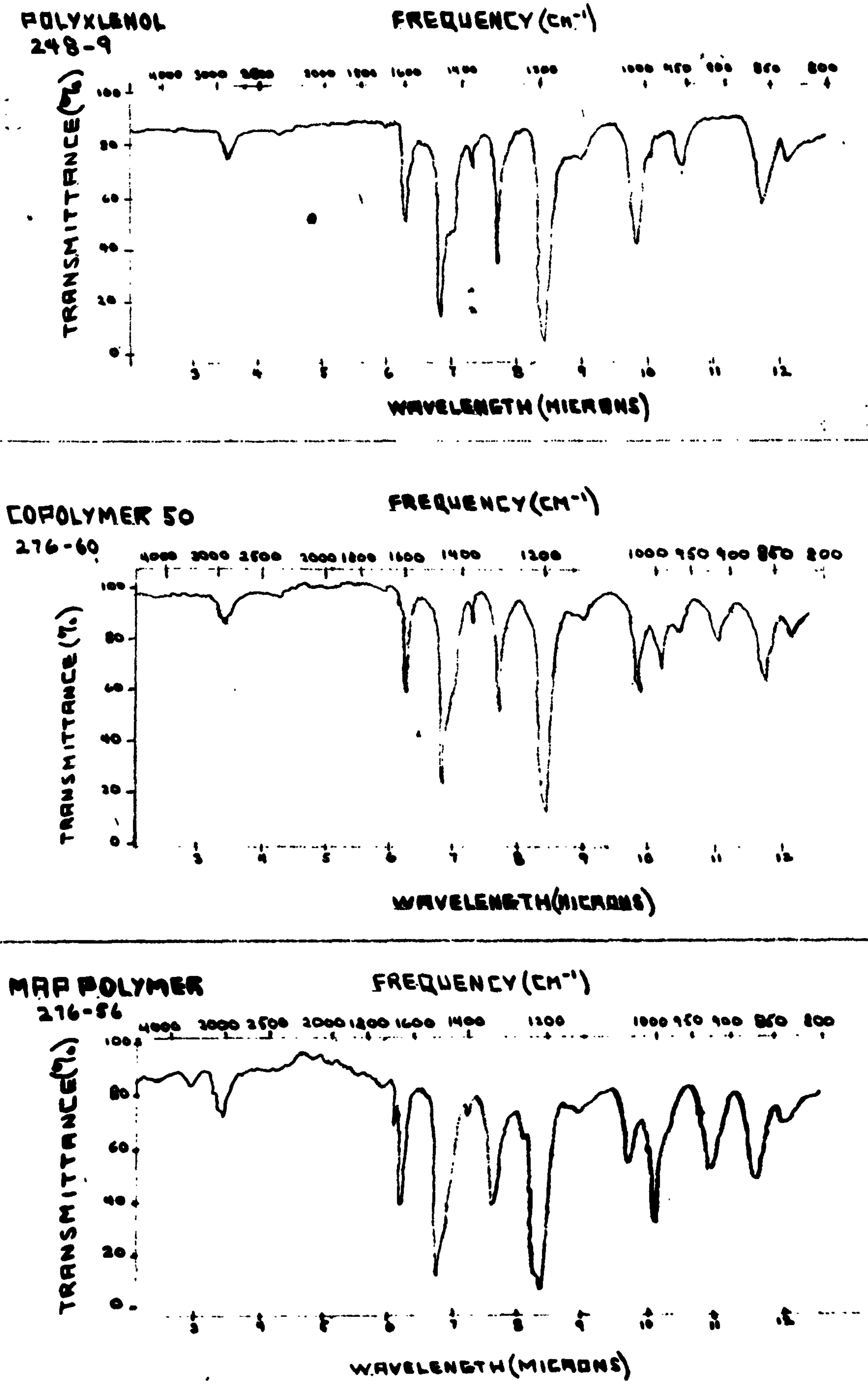
Based on the physical testing data later obtained, it was decided to concentrate on the 50:50 copolymer of xylenol and 2-methyl-6-allyl-4-bromophenol. Numerous runs are to be found in the Experimental Section. Here again the purity of the allyl derivative is essential to give a high molecular weight product.

5. POLYMERIZATION OF 2-METHYL-4-BROMO PHENOL

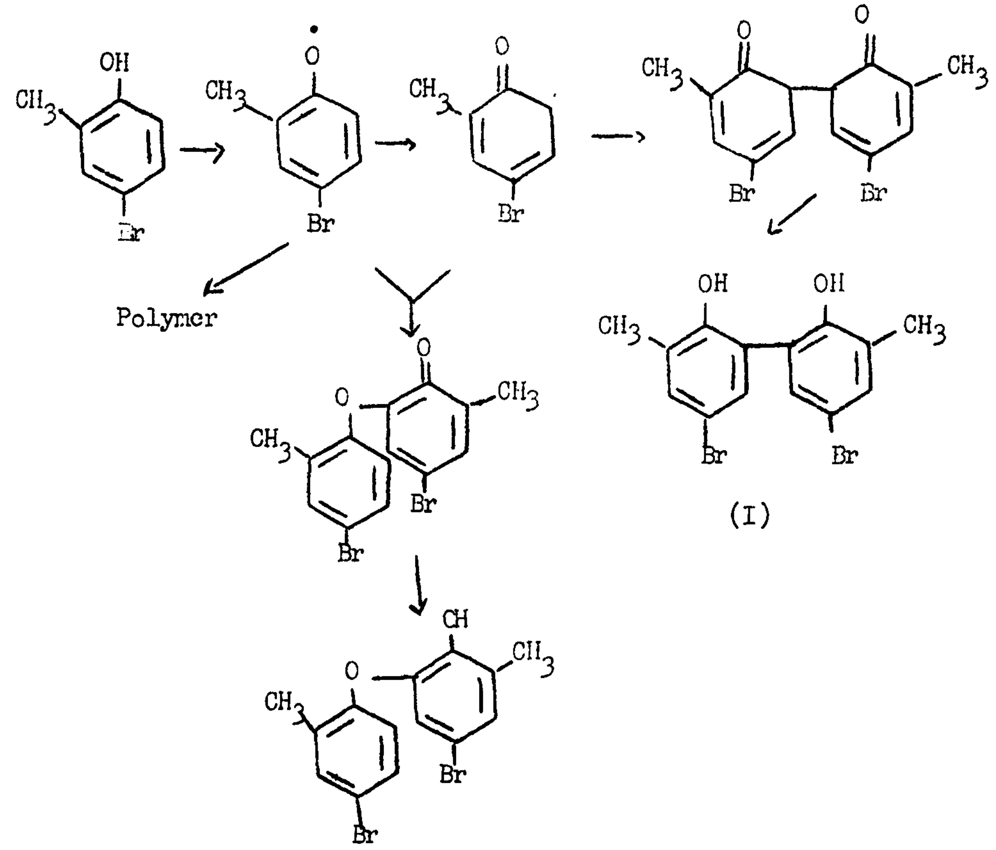
While Hay at General Electric and Price at University of Pennsylvania have reported that 2-methyl-4-bromo phenol could not be polymerized, it was of interest

FIG. I

I.R. SPECTRA OF POLYARYL ETHERS



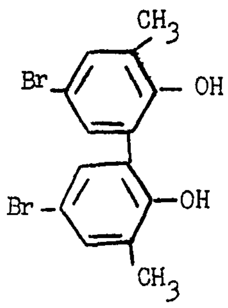
for us to see what could be isolated in the polymerization reaction. In particular, if it were possible to isolate compound (I) according to the following postulated mechanism:



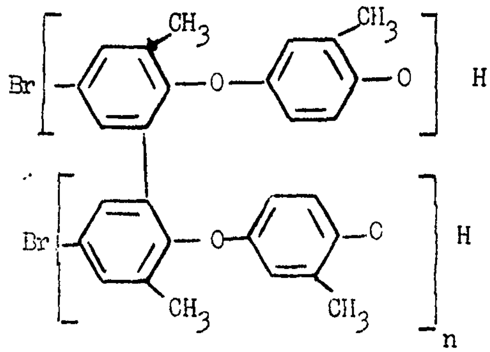
(I)

(II)

The preparation of "ladder" type polymers is known to further enhance the thermal stability generally. We have tried to extend this to the polyphenylene oxide type, thus:

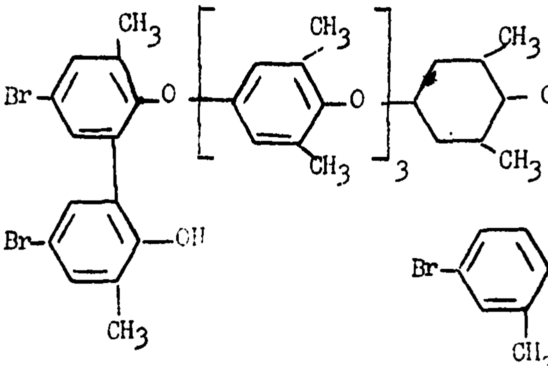


(I)

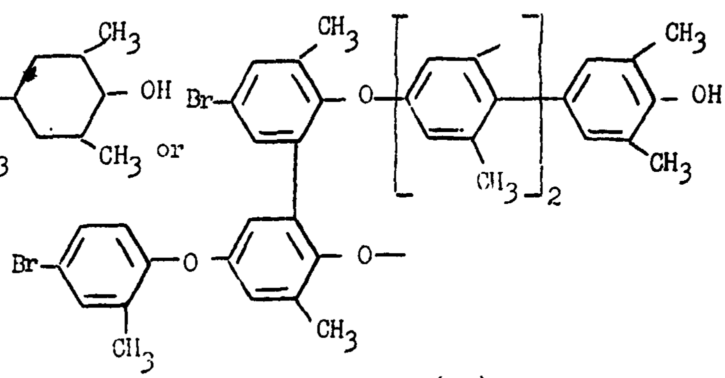


A "Ladder" Polymer (IV)

The idealized structure IV was not realized in the present trial, as the polymer isolated had relatively high Br content 23.29%. Based on the bromine analysis and infrared spectra, the polymer isolated can be assigned structures V or VI, or



or



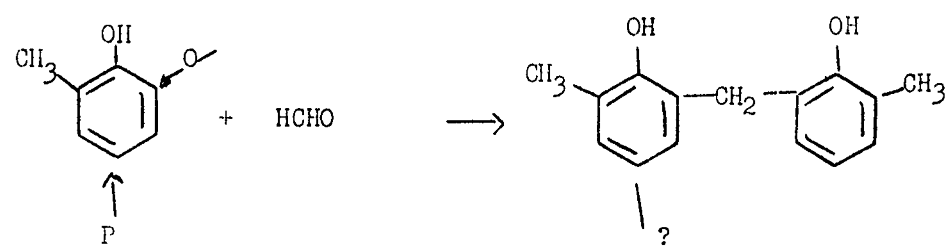
(V)

(VI)

variations similar to them.

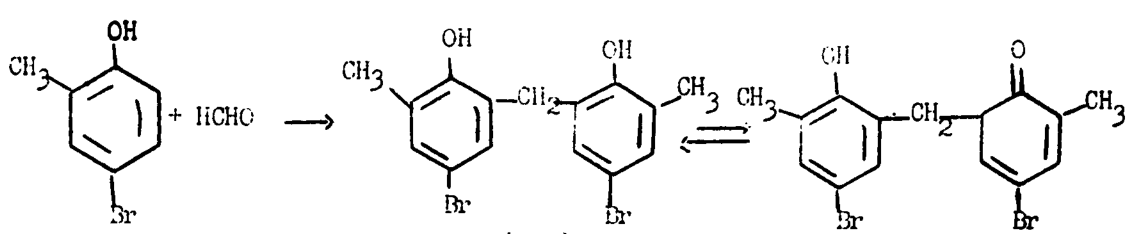
6. PREPARATION OF 4,4'-DIBROMO-2,2'-DIMETHYL-6,6'-DIMETHYLENEPHENOL

In the final report of the last contract period, the preparation of the "o-cresol novolac" dimer was mentioned from the reaction of o-cresol and formaldehyde. As it is obvious that such reaction of formaldehyde would take place at both the o- and p-positions, the structure of the resultant product is less certain and the assignment has now been found to be incorrect:



(VII)

As the "novolac type" polyphenylene oxide would be expected to enhance thermal stability and better adhesion, re-examination of the preparation of this type of polymer was considered worthwhile. The preparation of 4,4'-dibromo-2,2'-dimethyl-6,6'-bismethylene phenol (VII) was deemed necessary in order to provide an unambiguous starting material for subsequent polymerization. This was accomplished by the use of a similar procedure whereby Beaver[1/] has prepared the corresponding chloro-substituted compound:



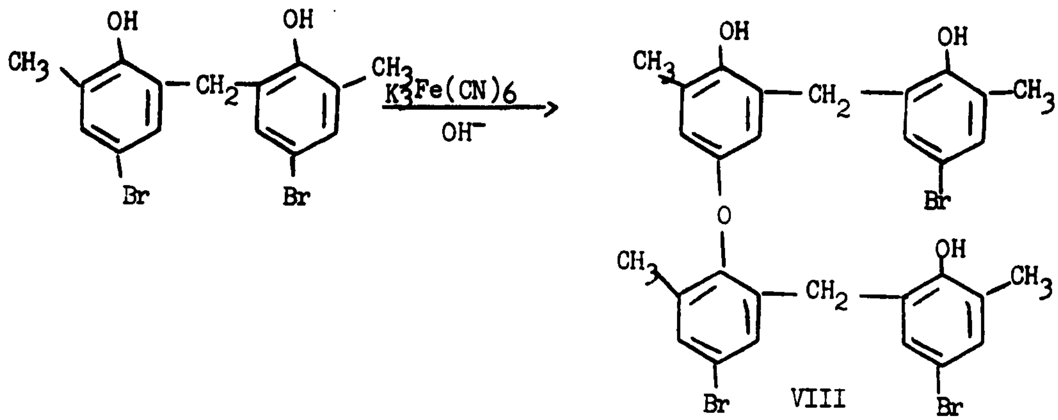
(VII) (VIIa)

VII prepared by this method has a melting point of 190-192° C., which is almost

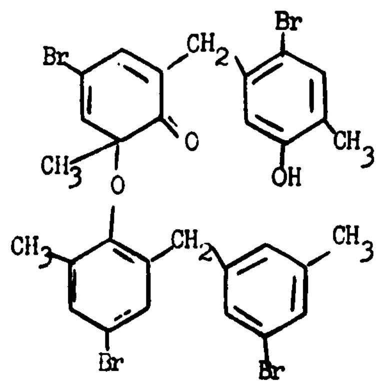
50° C. higher than that reported by us in the Final Report in the last Contract. The assignment previously made was therefore proven to be incorrect. The infrared spectra of VII was taken in its solid state (see Experimental Section). It is of interest to note a weak carbonyl band at 5.8 μ which can be attributed to the presence of structure VIIa.

Attempted polymerization of 4,4'-dibromo-2,2'-dimethyl-6,6'-bismethylene phenol was carried out in the usual manner. However, the anticipated polymer was not obtained. Instead, a yellow compound which melted around 250° C. was isolated. This compound has almost an identical infrared spectra to that of the starting material except an additional 6.10 μ weak band that can be assigned to the Ar-O-group. Based on this evidence and the bromine analysis (34.22%) this product has been assigned the structure VIII which has theoretical Br of 34.7%. The alternate ketonic structure IX is ruled out because of the bromine analysis, even though the presence of a tautomer such as VIIIa in its solid state is still possible as there is present a weak carbonyl band at 5.80 μ

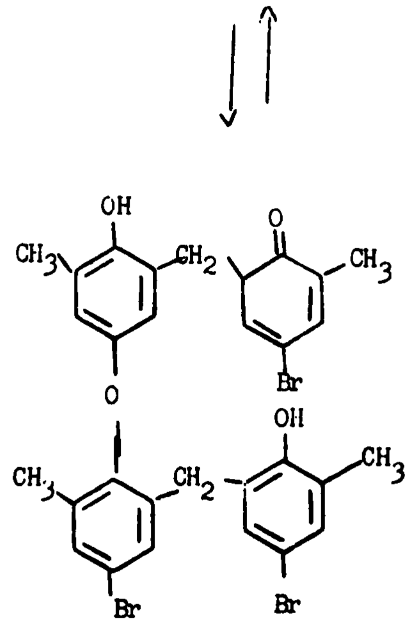
(formula on following page)



VIII



IX

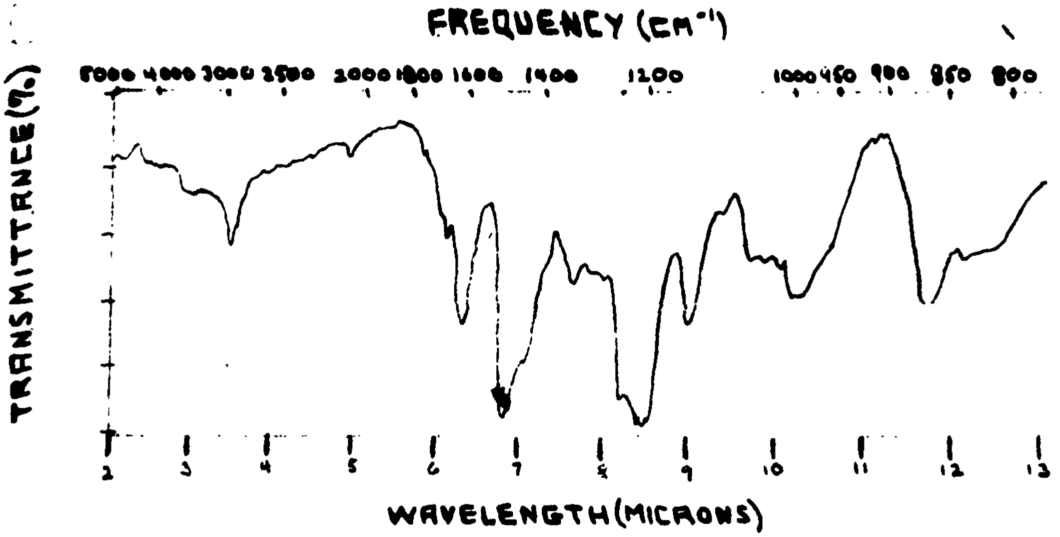


VIIIa

POLYARYL ETHER FROM
2-METHYL-4-BROMO-XYLENOL

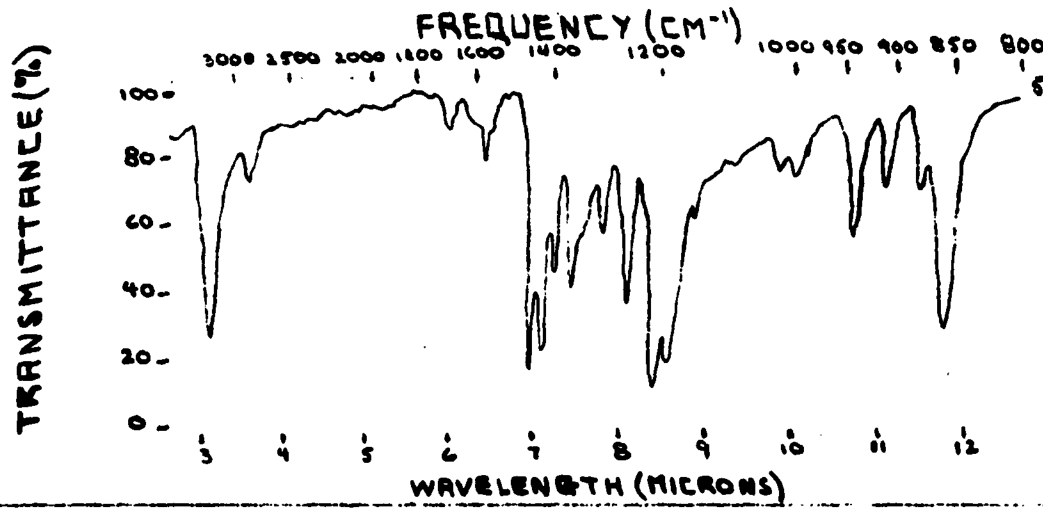
FIG. II

I.R. SPECTRA



DI(2-HYDROXY-3METHYL-5-BROMO)PHENYL METHANE

277-149 I

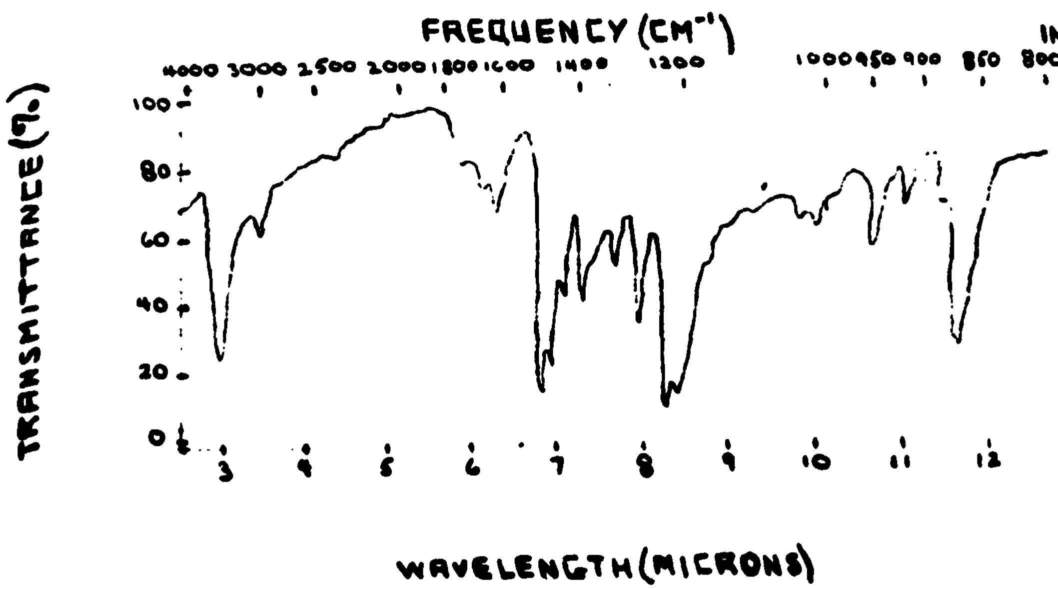


INSOLUBLE PRODUCT

FROM

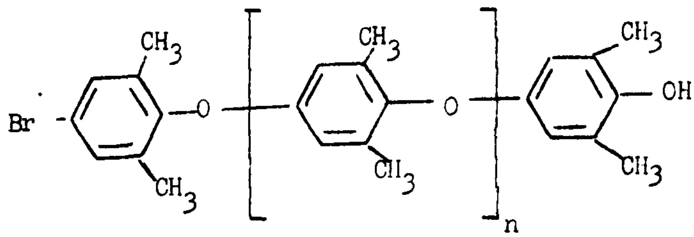
POLYMERIZATION

OF 277-149 I



7. MOLECULAR WEIGHT AND STRUCTURE OF THE POLYMERS

The molecular weights of the polyphenylene oxides have been determined so far by the bromine end group analysis. This has been assumed correct if the structure of the polymer can be represented by X:

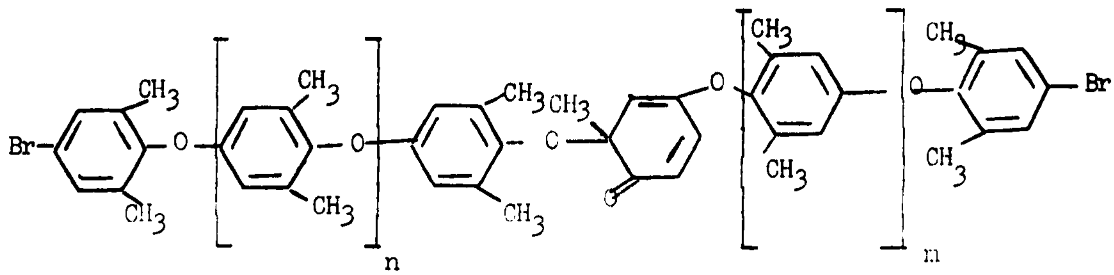


X

To verify this, intrinsic viscosity studies have been made on various representative samples, and the molecular weight calculated based on the equation[2/]

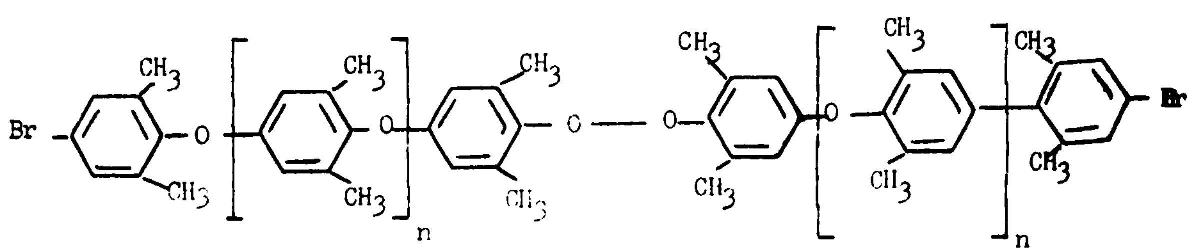
$$(\eta) = 3.8 \times 10^{-4} \quad M^{0.75}$$

The results are so different from that determined by the bromine end-group analysis that one has to assume that the assignment of X is no longer valid. The non-existence of OH band in the infrared spectra has been attributed so far so the high molecular weight. This assumption again could not be correct as even the lower molecular weight sample showed very little OH group present. At present, we are also in favor of a biradical coupling as a termination step, and the structure (XI) proposed by Price is a very probable one:



XI

This structure will bring the molecular weight determined by the intrinsic viscosity closer to that determined by the bromine end group analysis. However, the alternate structure XII cannot yet be ruled out in spite of the unusual peroxide linkage. It is our hope that, when time permits, some experiments will be carried out to settle these two probable structures. Other possibilities such as branching have also been considered by Dr. Price but evidence is equally lacking at the present time.



XII

8. PHYSICAL TESTING OF THE POLYMERS FOR ADHESIVE PURPOSES:

Because of the relatively high melting point of the polymers, it is difficult to adequately flow out the polymer and wet the stainless steel plate. In this period, some emphasis has been given to the development of an improved technique of applying the polymer to the surface. After testing various methods, the best reproducible result seems to have been obtained from the use of solvent coating first, followed by air drying for 7 days. A pre-impregnated laminated glass cloth was then used as an interlayer to insure a constant glue line.

By this technique, the best average for five trials of the polyxylenol gives 3150 psi at room temperature, and 1100 psi for the copolymer. However, at 500° F., the polyxylenol drops to 129 psi whereas the copolymer drops only to 265 psi. It is this latter data that provides good evidence that this allyl group is contributing to the thermosetting process in the copolymer. The drop to 25% strength at 500° F. can conceivably be improved by improving the initial strength at room temperature or by putting anchoring groups on the polymer to improve adhesion. The copolymers are lower in molecular weight and therefore some improvement may be possible. A systematic study of the crosslinking reaction may also considerably improve the efficiency of this reaction and thereby improve the resultant physical properties at elevated temperatures.

EXPERIMENTAL

1. CHEMICAL MODIFICATION OF POLYXYLENOL

A. Bromination of Polxylenol:

This is done essentially by a procedure similar to that reported previously. One hundred grams of polyxylenol (m.w. estimated on Br content 4580 or DP = 37) and 1 g. of benzoyl peroxide, 45 g. of N-bromosuccinimide admixed with 1 g. of benzoyl peroxide was added to the benzene solution at 60° C. The procedure was repeated to insure complete bromination after the reaction mixture was allowed to stand overnight. After removal of the succinimide, the product was precipitated from dry ice-cold methanol, washed and dried. There was a slight increase in molding temperature (ca. 450-500° F.) when compared against the starting polyxylenol. Anal. Br = 21.91%. As seen in the discussion, the assumption has now been corrected and about 18% of the available methyl groups have been converted to the bromomethylene group.

B. Reaction of Potassium Phthalimide with Brominated Polyxylenol (Sample No. 277-90):

In a 3-neck 1-liter flask equipped with stirrer, thermometer and a reflux condenser was added a solution of 65 g. of the brominated polyxylenol in 600 ml. of dimethyl formamide. This solution was now heated to 100° C. Upon cooling slightly to about 80° C., 30 g. of potassium phthalimide was added. The reaction mixture was now heated to 145° C. slowly in about two hours and allowed to stand overnight. After filtering off some insoluble matter, the solution was poured into chloroform (ca. 400 cc.). The chloroform solution was now washed with water to remove the salt. The chloroform solution was then concentrated to a small volume (ca. 100 ml.) and poured into 300 ml. of methanol to precipitate the product. Only 29.5 g. was obtained after washing and drying *in vacuo*. The product was found to have a molding temperature about 550° F. and analyzed to contain 2.27% N and 12.97% Br.

C. Crosslinking of Brominated Xylenol with Ammonia:

To a 5 g. sample of the brominated xylenol in 50 ml. of benzene was added with cooling 20 ml. of conc. ammonia. After warming the mixture with stirring, a gelatinous blue-green mass was obtained. After treatment with boiling water, the brown precipitate was filtered, washed again with hot water several times and dried to give 4.6 g. of a brown powdery material. This polymer was found to be infusible and brittle. It was analyzed to contain 1.08% N and 21.1% Br; therefore, the degree of crosslinking is rather low.

2. PREPARATION OF 2-METHYL-4-BROMO-6-ALLYL PHENOL:

In a well ventilated hood, 500 g. of 2-methyl-4-bromophenyl allyl ether was introduced into a well agitated 1-liter distillation flask provided with 5-inlets. The flask was well purged with nitrogen at room temperature while immersed in a magnetically stirred oil (Paraplex G25) bath heated to 235° C. As the reaction mixture reached 220° C., hexane was dropped onto its surface and allowed to flash off freely into the hood. The rate of addition was adjusted so as to maintain the temperature at 220° C. for half an hour. At the end of this period while a slow stream of nitrogen passed through, the flask was removed and cooled in boiling water first, then in air, till the contents reached room temperature.

Hexane (1500 ml.) was added and the contents cooled to about 10° C. The phenolic constituents were extracted with cooled Claisen's alkali (350 g. KOH in 200 ml. water + 1000 ml. methanol) using two extractions of 500 and 100 ml. respectively. (The dark color of the layer required a strong light to detect the interface of the first extraction.) The hexane layer was washed with 2 x 100 ml. water and the water combined with the alkaline layer. This was now cooled to about 10° C. and acidified with cooled 6N HCl (430 ml.). The precipitated oil was extracted with carbon tetrachloride and the extract washed with 3 portions of water, then vacuum stripped under a water aspirator at 120° C. The crude product was then redistilled under a short Vigreux column at 0.8 mm. to give 200 grams of a mid-fraction, b.p. 105-107° C. (yield 40 g.) n_D^{23} = 1.5745 (lit. n_D^{33} = 1.5695), D_4^{25} = 1.3831. Molar refraction: MR_D found 54.09; MR_D calcd. 53.60.

3. POLYMERIZATION OF 2-METHYL-4-BROMO-PHENOL:

A 9.7 g. sample of 2-methyl-4-bromophenol was added to 53 ml. of sodium hydroxide solution (112 g./liter) and 100 ml. of benzene. After purging with N_2 for half an hour and coolingto 7° C., 1.65 g. of potassium ferricyanide in 10 ml. water was added. 100 ml. of benzene was added and combined with another 50 ml. of chloroform extract. The solution was evaporated to dryness and extracted with hot benzene. The hot benzene solution was poured into four times its vol. of cold methanol. The precipitate was filtered, washed with methanol, and dried in a vacuum oven overnight at 35° C. to give 0.16 g. of product (ca. 3% yield). Anal: Br (found) 23.29%.

This polymer softened slightly when heated to 170° C., and can be molded around 450° F. Its infrared spectra indicates the presence of weak OH (2.80 μ) together with the following bands: 3.60 (CH), 6.15 (w, Ar-O-), 6.25 (m), 6.80 (s), 7.1 (shoulder), 7.60 (w), 8.20 (s), 8.40 (s), 8.95 (m), 9.60 (w), 9.80 (w) 10.10-10.30 μ (m), 11.70 μ (m), 12.10-12.25 (w). After molding, the product is too brittle to be of further interest.

From the alkaline extract, the major amount of the starting material can be recovered as a purplish-brown solid which can be purified by sublimation. The recovered product melted at 58-60° C. and did not give a mixed melting point depression when tested with starting material. The other impurities were not characterized.

4. PREPARATION OF 4,4'-DIBROMO-2,2'-DIMETHYL-6,6'-BISMETHYLENE PHENOL

2-Methyl-4-bromophenol (93.5 g., 0.5 M) and trioxymethylene (67.5 g., 0.25 M) were dissolved in 63 ml. glacial acetic acid. Under stirring, 23 ml. of conc. sulfuric acid was added dropwise. The temperature of the reaction mixture rose from room temperature to 85° C. and a muddy brown precipitate formed. Benzene (560 ml.) was added now together with .5 g. of Darco G60 to decolorize the mixture. After filtering off the charcoal while hot, the solution was now carefully washed with water, dried and concentrated to give 23.0 g. crude product, m.p. 171-180° C. After recrystallization from hot benzene, the purified product was obtained as lemon-yellow crystals which melted at 190-192° C. to almost black liquid.

Anal. Calcd. for $C_9H_{14}Br_2O_2$: C, 46.47; H, 3.66; Br, 41.41.
Found: C, 47.94; H, 3.73; Br, 41.34.

Its infrared spectra shows the following bands: 2.95 μ (s), 3.58 μ (vw), 5.80 μ (w), 6.25 μ (w), 6.80 μ (s), 6.95 μ (s), 7.10 μ (m), 7.30 (m), 7.65 (wm), 7.85 μ (m), 8.30 μ (s), 8.70 μ (s), 9.75 μ (uw), 9.90 μ (vw), 10.60 (m), 10.95 μ (w), 11.95 (w), 11.70 (m) and 12.90 μ (m).

5) Attempted polymerization of 4,4'-dibromo-2,2' dimethyl 6,6' bismethylene phenol

Into a 500 ml. flask was added 5 grams of the bismethylene phenol, 32 ml. 10% sodium hydroxide solution, 100 ml. water, and 60 ml. benzene with stirring. The contents were cooled to 9°C. while purging with pure nitrogen. One gram potassium ferricyanide dissolved in 6 ml. water was added. There was no exotherm as is usual with polymerization of 4-bromo 2,6-substituted phenols. After four hours during which the temperature was permitted to rise to 30°C. the reaction mixture was separated, the aqueous phase extracted with benzene. After washing the extract with water it was concentrated to 100 ml. No precipitation occurred on addition to 3 volumes of methanol (as occurs in the case of successful polymerizations). Evaporation to dryness yielded only a trace (0.3 g.) of solid I, not identified.

Acidification of the alkali soluble phase yielded two products, one soluble in chloroform (II) 1.6 grams and one insoluble in chloroform (III) 1.2 grams. The soluble fraction II after purification was identified as the starting bisphenol. The insoluble fraction III melted at 250°C., leaving a black residue. Infrared spectrum resembled the starting bisphenol except for a weak band at 6.25 μ (ArO-) Bromine content 34.22%, (calculated for the dimer structure in discussion,34.7%).

6) Copolymerization of 2-methyl-4-bromo-6-allyl phenol and 2,6-dimethyl phenol:

The procedure is essentially the same as that used in the preparation of the homopolymer and the results are summarized in Table I.

TABLE I

Copolymers From 2-Methyl-4-Bromo-6-Allyl Phenol and 4-Bromo-2,6-Dimethyl Phenol

276-		52	60	62	66
Mol % MBAP*		20	50	10	20
MBAP*	g.	2.9	6.4	1.34	5.8
Bromoxylenol	g.	9.4	5.6	1065	18.8
NaOH	g.	5.3	5.3	5.3	10.6
Water	g.	56.0	56.0	56	112
Benzene	ml.	100	100	100	200
$K_3Fe(CN)_6$	g.	1.65	1.65	1.65	3.3
Temp. initial	C°	7	4.5	7.5	7.0
Temp. final	C°	31	30	30.0	29.0
Time	hr.	3.5	1.8	3.7	2.2
Wt. of polymer	g.	6.6	7.1	6.6	14.4
Wt. yield of polymer	%	50.8	59.1	55.0	58.5
Bromine in polymer	%	2.95	3.1	2.3	-
M.Wt. Calcd. from above		2710	2580	3470	-
Molding temp. min.	F°	450	400	450	475 (C)
Unprecipitate material (A)	g.	0.4	0.2	1.1	0.2
Unconverted phenols(B)	g.	.05	-	-	-

Notes * 2-Methyl-4-bromo-6-allyl phenol
(A) By evaporation to dryness of benzene-methanol filtrate from the precipitation.
(B) By acidification of caustic layer, extraction, evaporation to dryness.
(C) Min. temperature at which polymer can be molded by compression on hot plate, observed at 25°F. increments.

After testing various samples, it was found that the copolymer 50:50 gives a tough product on curing. This ratio was therefore chosen for subsequent runs and enough samples were made in order to provide adequate testing and post-modification such as epoxidation. The runs are listed in Table II.

TABLE II

Copolymer 50 Preparation

Run No.	276-60	276-82	276-84	276-86	276-90	276-92	276-100	300-17	300-22
MBAP g.	6.4	25.6	6.4	6.4	6.4	6.4	23.2	6.4	6.4
MBAP Prepn.No.	7-122-2	7-142-2	7-142-2	7-122-2	7-142-1	7-122-2	7-122-2	7-142-3	7-142-3
Bromo-xylenol g.	5.6	22.4	5.6	5.6	5.6	5.6	20.3	5.6	5.6
NaOH g.	5.2	20.8	5.2	5.2	5.2	5.2	18.8	5.2	5.2
Water g.	56.0	224.0	56.0	56.0	56.0	56.0	206.0	56.0	56.0
Benzene	100.	400.	100.	100.	100.	300.	362.	100.	100.
$K_3Fe(CN)_2$g.	1.65	6.6	1.65	1.65	1.65	1.65	6.0	1.65	1.65
Temperature °C									
Initial	4.5	4.5	5.0	6.0	5.0	5.0	4.0	6.5	5.5
@ 3 min.	11.0	4.5	9.5	11.0	7.5	5.5	6.5	9.0	8.5
Polymer g.	7.1	24.8	6.3	6.4	4.0	6.9	25.5	7.2	6.7
Polymer, Theor.wt.g.	7.45	29.81	7.45	7.45	7.45	7.45	26.81	7.45	7.45
Phenolic by-prod.(A) g.	-	3.5	-	0.1	0.4	0.1	0.7	0.3	0.1
Non-Phenolic by-prod.(B) g.	0.2	-	0.4	0.4	1.0	0.2	0.3	0.2	0.1
Bromine in polymer %	3.1	5.1	4.17	2.81		3.53	3.02	4.39	2.77
Intr.visc.(n)	.31	.11	.14	.286	.093	.140	.282	.375	.390
Mold Temp. min.°F.	400	250	350	400	300	300	400	400	400

Notes: (A) Isolated from caustic layer after extraction of polymer.
(B) Isolated from mother liquor after precipitation of polymer into methanol.
MBAP = 2-methyl-4-bromO-6-allyl phenol

7. **Physical Testing Results:**

Comparison of Polyxylenol and "Copolymer 50":

Polyxylenol (Lot 248-56C) was applied to the surface as seen in the accompanying Table III. The polyxylenol was cured by heating to 290-300° C. The "copolymer 50" (276-100) was applied in the manner described and cured by heating to 250-260° C. The pressure used during the curing on the slabs was 200 psi.

TABLE III

Room Temp. Test

Sample No.	Method of Application	Strength	No. of Samples Used
284-56C (polyxylenol)	Powder	1240 psi	5 samples
276-100 (copolymer_50)	"	1630 "	5 samples
284-56C	Brushed on	1530 "	5 samples
276-100	" "	200 "	3 samples - 2 samples fell apart
Failure was cohesive - coating either not heavy enough or material does not flow enough			
248-56C	Brushed on + cloth	3150	5 samples
276-100	" " " "	1100	5 samples

500° F. Test:

Sample No.	Method of Application	( )* No. of Samples 1/2 hour	3 min.
248-56C	Powder	81 (3)*	267 (2)
276-100	"	36 (2)	52 (1)
248-56C	Brushed on	49 (3)	206 (2)
276-100	" "	24 (3)	0 (2)
248-56C	Brushed on + Cloth	129 (3)	129 (2)
276-100	" " " "	265 (3)	78 (2)

8. Molecular Weight Determination:

The intrinsic viscosities of some typical samples were determined and their molecular weight calculated by an empirical equation given by Dr. C. C. Price[2/] (who obtained the equation from a curve supplied by Dr. A. S. Hay). The discrepancy between the M.W. obtained by this method and that obtained by the bromine analysis are given in Table IV.

TABLE IV

Molecular Weight of Polymers

Preparation No.	Type	Br %	M.Wt. (b)	Intrinsic Viscosity [η]	M. Wt. (c)	Softening Point Min.°F. (d)
276-56	Homopolymer of MAP (a)	3.54	4,520	0.160	2.95×10^3	200
276-62	Copolymer-10(e)	2.30	6,940	0.387	1.05×10^4	450
276-52	Copolymer-20 (f)	2.95	5,420	0.275	6.46×10^3	450
276-60	Copolymer-50 (g)	3.10	5,160	0.310	7.86×10^3	400
248-56a	Polyxylenol (h)	1.06	7,550	0.460	1.32×10^4	500
248-56c	Polyxylenol (h)	0.87	9,200	0.540	1.59×10^4	550
248-9	Polyxylenol (h)	1.12	7,150	0.420	1.13×10^4	450
277-88-1	Polyxylenol (h)	5.57	1,440	0.093	1.52×10^3	350
226-20-2	Polyxylenol (i)			1.24	5.90×10^4	600

(a) MAP = 2-methyl-4-bromo-6-allyl phenol
(b) Based on assumption of two bromine end group per mole
(c) Based on $[\eta] = 3.8 \times 10^{-4}\ M^{0.75}$ given by Dr. C. C. Price[2/] "Polyethers XIII", manuscript submitted to J. Poly.Sci. Aug. 1, 1961
(d) Minimum temperature at which the polymer can be molded by compression on hot plate, observed at 50° F. temperature increments.
(e) 10 mole % 2-methyl-4-bromo-6-allyl phenol and 90% 2,6-dimethyl-4-bromo phenol
(f) 20% MAP (by mole)
(g) 50% MAP (by mole)
(h) Prepared from 4-bromo-2,6-dimethyl phenol by the Price method.
(i) Prepared from 2,6-dimethyl phenol by the Hay method.

9. Effect of Aging on Minimum Molding Temperature of the Allyl-Containing Polymers:

The results are best summarized in the following Table (V).

TABLE V

Effect of Aging on Minimum Molding Temperature
Allyl-Containing Polyethers

Prepn. No.	Class	Orig. Molding Temp. °F.	Molding Temperature - After Aging			
			Days	° F.	Days	°F.
276-18	MAP	200	45	200	71	200
276-35	MAP	200	34	200	61	200
276-38	MAP	250	33	250	59	250
276-42	MAP	150	30	200	49	200
276-56	MAP	200	23	250	49	250
276-52	Copolymer 20	450	27	450	53	450
276-60	Copolymer 50	400	22	400	48	400
276-62	Copolymer 10	450	21	500	47	475
276-66	Copolymer 20	475	20	500	46	475

Notes: MAP = polymer from 2-methyl-4-bromo-6-allyl phenol
Copolymer (Numbers represent calculated molar parts of the above phenol in a mixture with 2,6-dimethyl-4-bromo-phenol).

The molding temperatures are the minimum temperatures at which the polymers can be molded as measured by tests at 25° F. increments.

REFERENCES

1. D. S. Beaver and R. P. Stoffel, J. Am. Chem. Soc. 74, 3410 (1952)

2. Acknowledgement is due to Professor C. C. Price for making available his manuscript for J. Poly. Sci. prior to its publication, where he gives this equation.